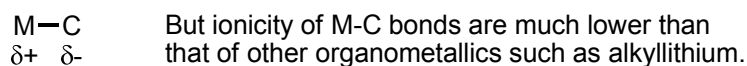


**Contents** (ref: 『大学院講義(I)』 p.341-384)

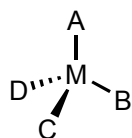
- 8-2. Chemistry about Group 14 Elements
- 8-3. Chemistry about Group 15-17 Elements
- 8-4. Ate Complex and Hypercoordinate Compounds
- 8-5. Reaction of Carbon-Metal Bonds

**8-2. Chemistry about Group 14 Elements**

**Si, Ge, Sn, Pb** : More electronically positive than carbon (C)



**8-2-1. Substitution at Group 14 Elements**



(M = group 14 elements)

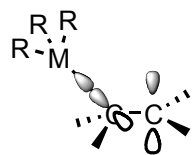
- They have chirality (of course, if A~D are all different).
- Nucleophilic substitution ( $S_N2-M$ ) is much faster than carbon.
- That's because of a stable 5-coordinate intermediate.
- It means stereochemical inversion does not always occur.

| Tendency of stereochemical inversion or retention |                  |                  |
|---|------------------|------------------|
|   | <u>inversion</u> | <u>retention</u> |
| leaving group :                                   | highly polarized | low polarized    |
| nucleophile :                                     | soft             | hard             |

**8-2-2. Effects of Substituents**

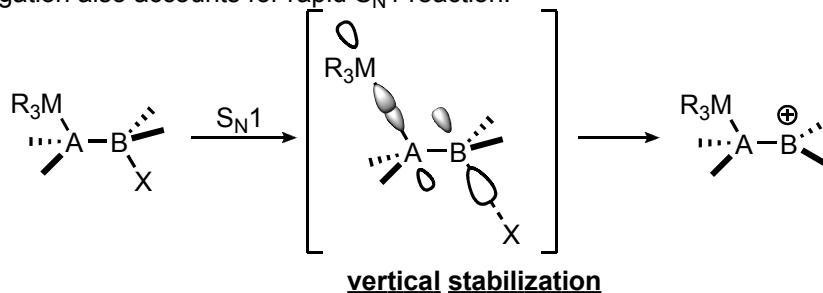
$\beta$  effect:

Trimethylsilyl (TMS) group shows high electron donating effect when it is at a carbon adjacent to a  $\pi$ -electron system (such as benzylic or allylic).

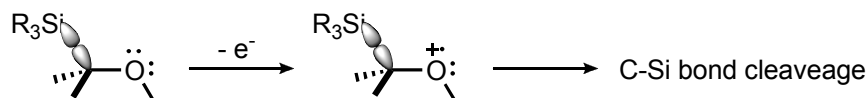


It's due to **hyperconjugation** between M-C bond's  $\sigma$ -orbital and  $\pi$ -orbital.

Hyperconjugation also accounts for rapid  $S_N1$  reaction.

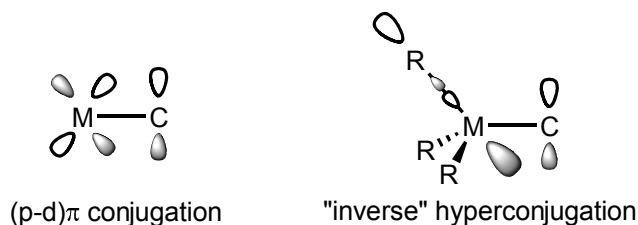


$\beta$ -effect works against lone pair of oxygen/nitrogen at  $\beta$ -position to decrease oxidation potential.



### $\alpha$ effect:

- Silyl group combined directly to  $\pi$ -electron system shows relatively strong electron withdrawing conjugative effects.
- This electron withdrawing nature is measured in hyperfine coupling constant of radical anion of mono-substituted benzene.
- Origin of this effect is considered to be  $\sigma^*$  orbital (pseudo  $\pi^*$  orbital) of Si-C bond.  
**("inverse" hyperconjugation)**  
(Traditionally, it's considered to be d- $\pi$  conjugation of Si.)



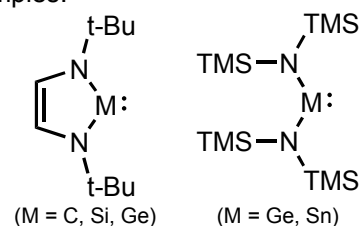
### 8-2-3. Unstable Species of Group 14 Elements

Group 14 elements can form chemical species like carbon.

#### 2-coordinate chemical species

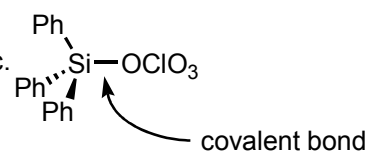
- Silyrene, germyrene, and stannyrene are generally unstable like carbene.
- Silyrenes or germyrenes are **all singlet** unlike carbenes.
- Silyrene shows similar reactivity with singlet carbene, but not react with C-H bonds or C-C bonds.
- They form Lewis pair with ethers or amines.

examples:



#### Cations

3-coordinate silyl cation is too unstable and highly electrophilic.

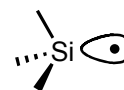


#### Anions

3-coordinate silyl anion is stabilized by aromatic substituent like phenyl group. Stabilization of silyl anion by phenyl group is considered to be due to  $\pi$  inductive effect.

#### Radicals

Radical reductions by silyl hydride or stannyl hydride are well-known. Pyrimid inversion of silyl radical is slow because of unplanar structure.



#### Double bonds

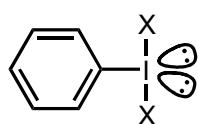
$H_2M=MH_2$  are not planar and take trans-bent structure. These double bonds are considered to be donating-bonding between two 2-coordinate species.



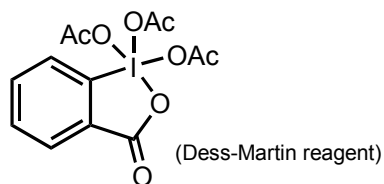


### 8-3-3. High-Period Group 17 Elements

High-period halogens (especially iodine) form stable high-coordinate compounds.



organoiodinane  
(X = F, Cl, Br, etc.)



organoperiodinane  
(Dess-Martin reagent)

### 8-3-4. Organofluorine Chemistry

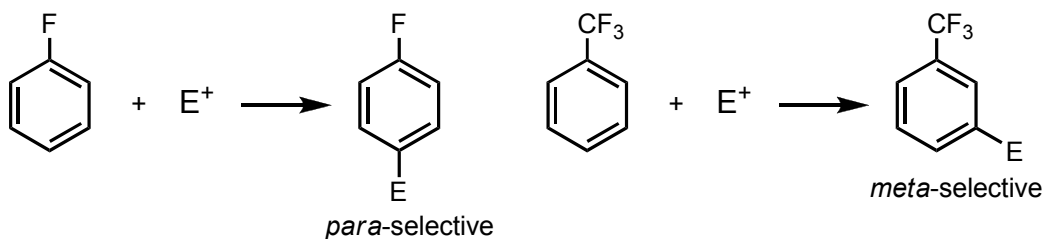
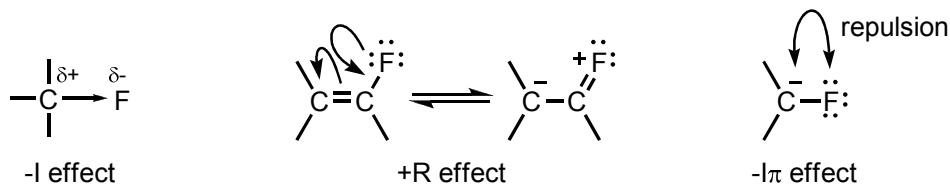
#### Different features from other halogens

- Unreactive for halogen-lithium exchange (due to small atomic radius = unstability of high-valent species).
- Most electronegative element.
- "van der Waals radius" similar to that of H offers intriguing property for bioactivity.

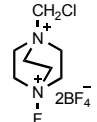
#### Electronic effects

- via  $\sigma$ -bond  
strong electron-withdrawing inductive effect (-I effect)
- via lone pair of p-orbital  
electron-donating resonance effect (+R effect) and  $\pi$ -inductive effect (+I $\pi$  effect)

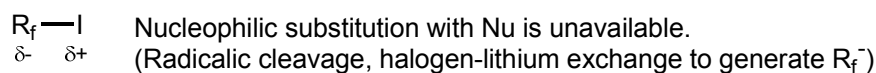
*These orthogonal effects determine the reactivity of fluoride compounds.*



#### Fluorination reaction

- Nucleophilic fluorination : KF, Et<sub>2</sub>NSF<sub>3</sub>, etc.
- Electrophilic fluorination : FClO<sub>3</sub>, CF<sub>3</sub>OF, , etc.

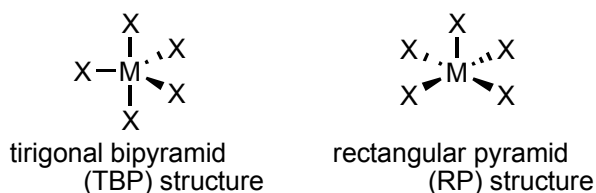
#### Perfluoroalkylation reaction



## 8-4. Ate Complex and Hypercoordinate Compounds

"Ate complex" = anionic complex salt having hypercoordinate central atom  
 "Hyper coordinate compounds" = central atom has more electron over Octet Rule.

### 8-4-1. Bonding of 5-Coordinate Compounds



**Muetterties Rule** : More electronegative ligands take **apical** position and more electropositive ligands take **equatorial** position in TBP structure.

### 8-4-2. Bonding of 6-Coordinate Compounds

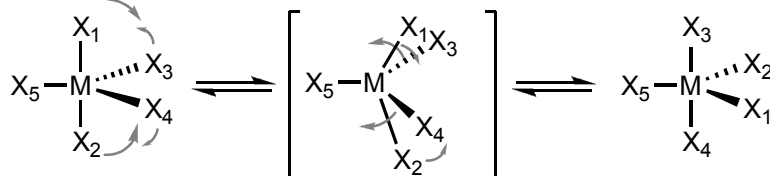


### 8-4-3. Isomerization of Ate Complex

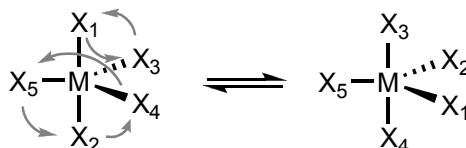
#### Isomerization of 5-coordinate compounds

Two hypothetical mechanism is probable:  
 pseudorotation mechanism (Berry)  
 turnstile rotation mechanism (Ugi)

- pseudorotation mechanism



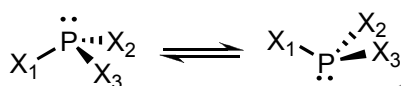
- turnstile rotation mechanism



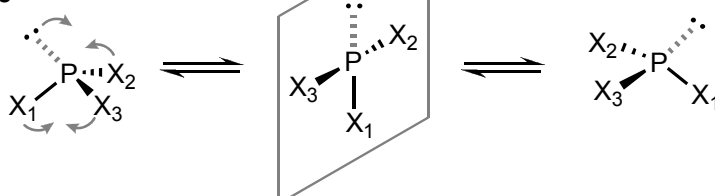
The former is enagetically advantageous.

#### Isomerization of 3-coordinate compounds

- vertex inversion

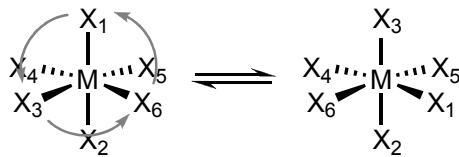


- edge inversion

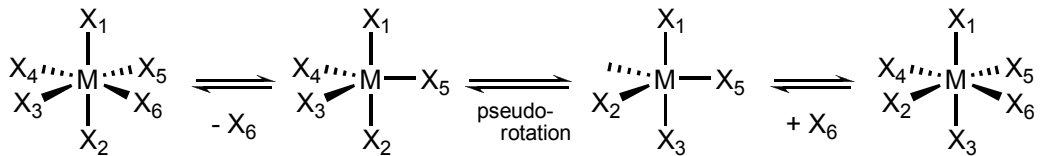


## Isomerization of 6-coordinate compounds

- *twist mechanism (Bailor)* : few examples



- *multisteps mechanism* : many examples

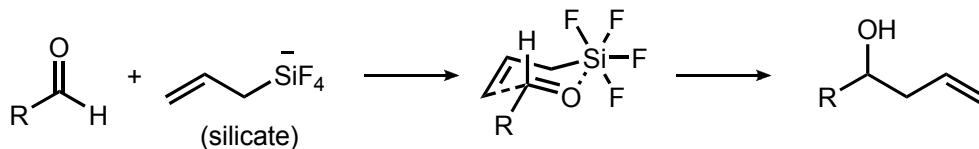


### 8-4-4. Reactivity of High-Coordinate Compounds

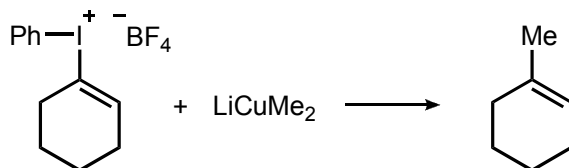
Roughly divided into two patterns:

- Organo-substituent of e-rich central atom works as nucleophile.
- Organo-substituent works as electrophile and e-rich central atom works as LG.

Example of the former case



Example of the latter case

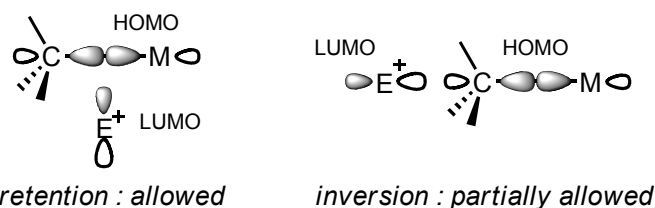


Other examples : Peterson, Wittig, Corey-Chaykovsky, etc.

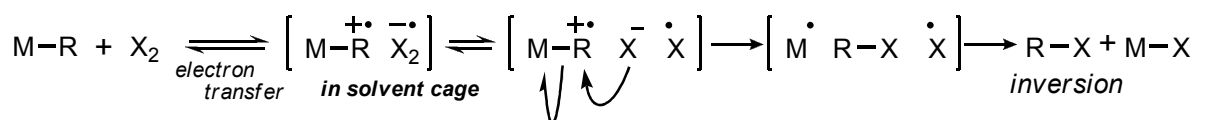
## 8-5. Reaction of Carbon-Metal Bond

### 8-5-1. Reaction Mechanism

S<sub>E</sub>2 reaction (1 step): stereochemical retention or inversion



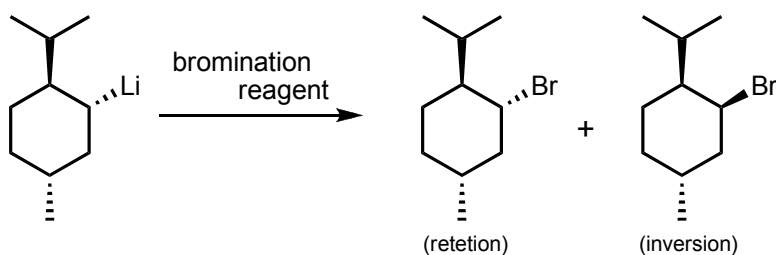
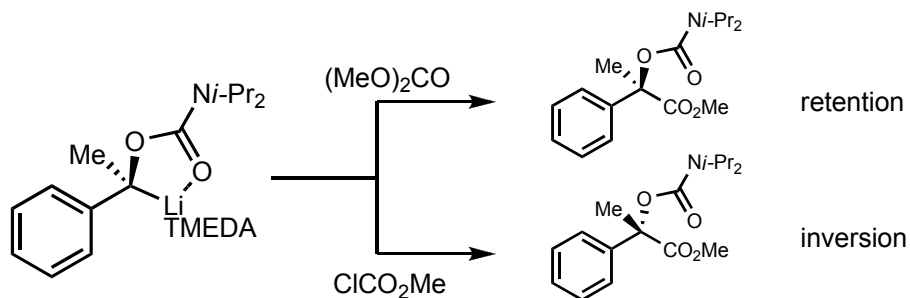
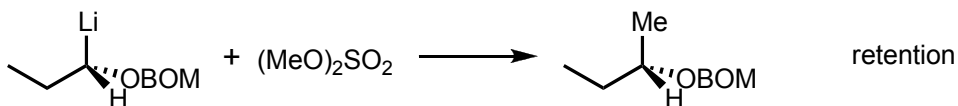
Mechanism via electron transfers (multi steps) : stereochemical inversion or racemization



or *racemization* if these intermediates are diffused (not in solvent cage)

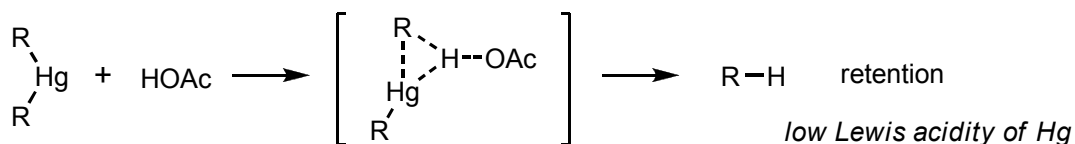
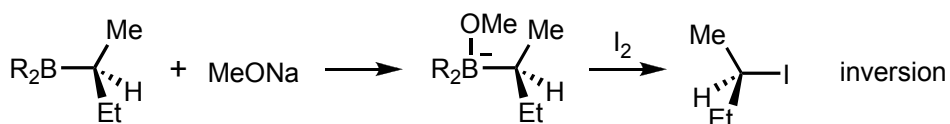
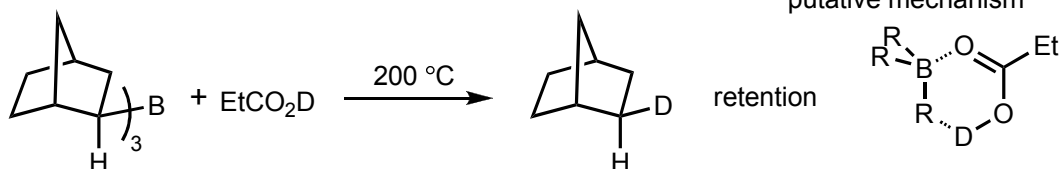
### 8-5-2. Alkyl-Metal Bonds

#### Organometallics of Group 1, 2

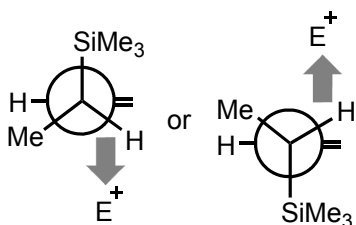
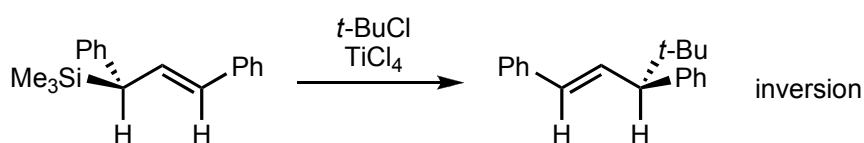


with  $\text{Br}_2$  : 25 : 75  
 with  $\text{BrCH}_2\text{CH}_2\text{Br}$  : 97 : 3

#### Organometallics of Group 12, 13, 14



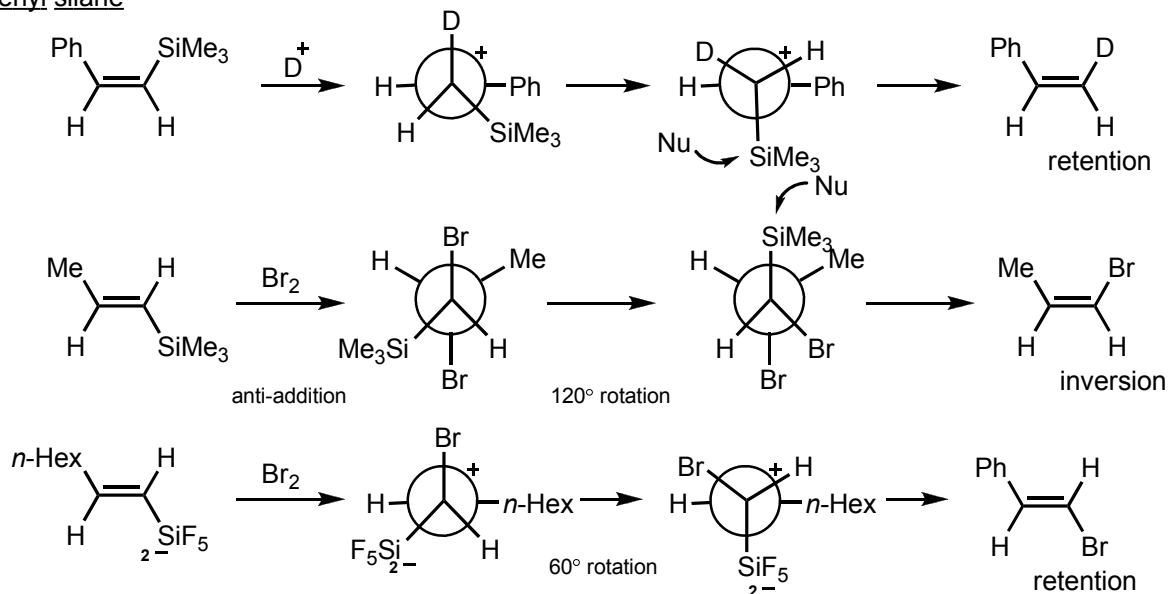
### 8-5-3. Allyl-Metal Bonds



Strong interaction between alkene's  $\pi$ -orbital and C-Si bond's  $\sigma$ -bond offers vertical position of Si group.

8-5-4. Alkenyl-Metal Bonds

Alkenyl silane



Alkenyl borane

